Partial Density of States of B-2*p* in AlB_2 type Compounds

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Since the discovery of superconductivity in MgB_2 with a transition temperature, T_c, of 39 K by Nagamatsu *et al.*,[1] large number of researches from experimental[2-5] and theoretical point[6-12] of view have been performed on this compound and on a series of isostructural diborides. Although there are many experimental results that suggest holes in B-2*p*σ band with a strong electron-phonon coupling play important roles in the superconductivity of MgB_2, the reason for the high value of T_c is not clear.

In order to clarify the mechanism of high T_c superconductivity in MgB_2, it is important to investigate the difference in the electronic states between MgB_2 and other isostructural diborides. In the present study, we present X-ray emission (XES) and absorption spectra (XAS) near the boron (B) *K* edge in MB_2 (*M*=Mg, Al, Ta and Nb). AlB_2 and TaB_2 are not superconductors and a superconductivity in NbB_2 is controversial now. XAS was measured by both the total fluorescence yield (TFY) and the total electron yield (TEY) measurements at the same time. The reason we choose boron is because the band calculations for MgB_2 indicate that the bands near the Fermi energy are mainly composed from boron 2*p* orbitals.

The commercial specimens from Rare-Metallic Co. characterized by powder X-ray diffraction and dc-magnetization measurements, were used as samples of MB_2 (*M*=Mg, Al, Ta and Nb). The dc magnetization measurements indicate that the superconducting transition temperature of about 38 K for MgB_2 sample, and no superconducting transition for TaB_2, NbB_2 and AlB_2 above 1.8 K. The soft X-ray emission and absorption spectroscopies were performed at BL-8.0.1 of Advanced Light Source (ALS) in LBNL. In order to calibrate energy, XAS by TEY were also measured at the well calibrated beam line BL- 6.3.2 of the ALS.

Figure 1(a) shows XES (○) and XAS (●) of MgB_2. The sharp decrease of XES and XAS at about 186.3 eV is attributed to the Fermi energy measured from 1*s* core level. The solid line in Fig. 1(b) is the boron PDOS obtained from a band structure calculation[10], where we have taken into account the effect of the instrumental resolution by gaussian broadening. The intensities of experimental XES and XAS in Fig. 1(a) are scaled to the theoretical PDOS in the energy region, $E \leq 182$ eV for XES and $187 \text{ eV} \leq E \leq 191$ eV for XAS. The sum of the experimental XES and XAS are also plotted in Fig. 1(b). It can be seen that the overall feature of both XES and XAS, including the existence of a large PDOS around the Fermi energy, are remarkably well reproduced by the band structure calculation, enabling us to attribute each observed structure to *p*π and/or *p*σ states. Namely, the existence of peaks A and B, which is consistent with recent studies[3], are characteristic of bonding *p*σ states. The region C in the energy range from 187 to 191 eV is attributed to the *p*π states. A sharp peak D at about 192 eV in XAS is reported to be a resonance peak of *p*π* state[3], and also corresponds to antibonding

$p\sigma^*$ state predicted by a band calculation. Thus peak D contains both the $p\sigma^*$ and resonance state of $p\pi^*$ states.

Figure 1(c) shows XES and XAS of AlB_2. The intensity of XES is normalized so that the area intensity coincides with that for MgB_2 below E_F, while the intensity of XAS is scaled so that the intensity in the high energy region, $E \geq 198$ eV, coincides with that for MgB_2. In the high energy region, XAS shows no strong characteristic peaks. A broad tail of XES below 183 eV is similar to that of MgB_2, but the value of E_F shifts to be 187.5 eV. The form of XES of AlB_2 is broad compared to that of MgB_2. Figure 1(d) shows experimental PDOS derived from the sum of XES and XAS. A dip is observed at about 188 eV near the Fermi energy, indicating that the B-2*p* PDOS around the Fermi energy is drastically reduced compared to that in MgB_2. This is the major difference between MgB_2 and AlB_2.

This difference can be understood from results of the band calculation for AlB_2.[12] Namely, there are several factors that make the boron 2*p* PDOS around the Fermi level in AlB_2 much smaller than in MgB_2. First of all, the bonding σ bands, whose tops are located above the Fermi level in MgB_2, are fully filled in AlB_2. Secondly, the Fermi level is located at a point where the top of the bonding and bottom of the antibonding π bands touch with each other at the *K* point. If the system were purely two-dimensional, this would be a point where the DOS vanishes linearly as a function of energy. Although the π band is three dimensional, the above two-dimensional property remains because the system is anisotropic.

The difference between MgB_2 and AlB_2 can qualitatively be understood within a simple rigid band model, namely by simply shifting the Fermi energy as mentioned above. To be more precise, there are some quantitative differences, whose origin seems to lie beyond a rigid band picture. Namely, in AlB_2, the intensity of XAS just above the dip is larger than that in MgB_2, while the intensity of peaks A and D is suppressed. Looking again into the band calculation results, these features may be attributed to the increase of three dimensionality in AlB_2.

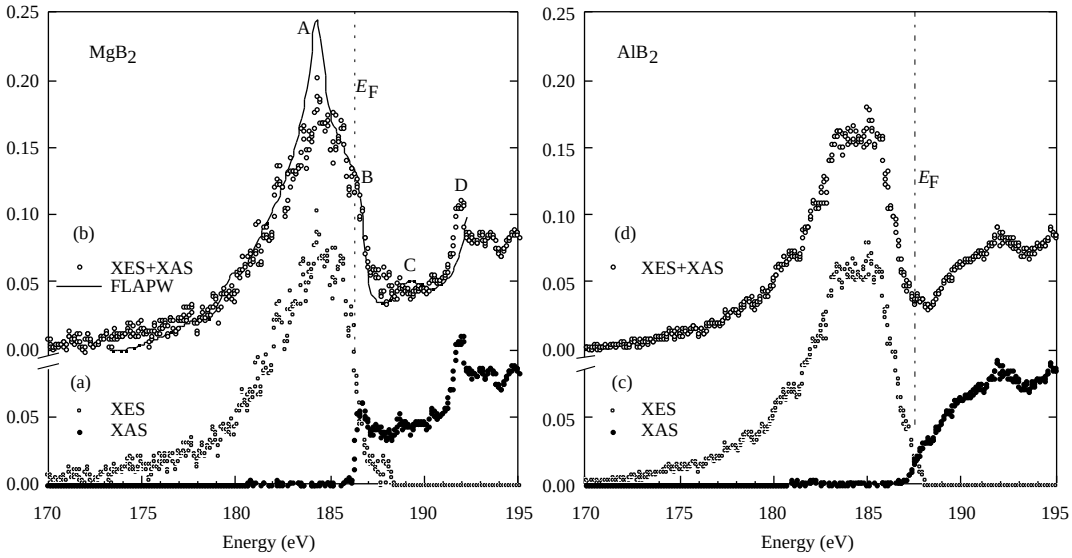

Fig.1 (a) The observed XES (○) and XAS (●) spectra of MgB_2. (b) The sum of XES and XAS (□) and the theoretical PDOS (solid line) derived from FLAPW method broadened with experimental resolution. (c) The observed XES (○) and XAS (●) spectra of AlB_2. (d) The sum of XES and XAS (□).

The XES and XAS of TaB_2 and NbB_2 are similar to those for AlB_2 except for a shift in

the Fermi energy up to 188.6 eV, owing to a larger band filling compared with AlB_2. The B-2*p* PDOS at the Fermi energy of TaB_2 is similar to that for AlB_2, so if TaB_2 is indeed superconducting, the difference between these two compounds should lie elsewhere. In NbB_2 compound, the Fermi energy is almost the same as that of TaB_2, but a considerable amount of DOS below the Fermi energy is observed. In both compounds, TaB_2 and NbB_2, band calculation suggests a strong hybridization between B-2$p\pi$ and Ta-5*d* or Nb-4*d* electrons. The characters of the states near the Fermi energy in TaB_2 and NbB_2 cannot be identified from the present results.

To summarize, the most characteristic feature in MgB_2 as compared to other related materials is the large B-2*p* PDOS around the Fermi level. Since this is partially attributed to the existence of the $p\sigma$ bonding band at the Fermi level, one may be tempted to consider that the $p\sigma$ band plays a crucial role in the occurrence of superconductivity in MgB_2.[8] This is indeed probable, but is not necessarily the case because the $p\pi$ band filling is also different between MgB_2 and other materials as mentioned above, which should result in a large difference in the shape of the $p\pi$ band Fermi surfaces. Let us note that the shape of the Fermi surfaces can play an essential role in the occurrence of superconductivity. For example, in those mechanisms that exploit nesting between the Fermi surfaces of bonding and antibonding π bands, the shape of the Fermi surfaces (namely the π band filling) is crucial. We believe that further studies are necessary to clarify this point.

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REFERENCES

[1] J. Nagamatsu et al.: Nature (London) **410**, (2001) 63.
[2] Z. Kurmaev et al.: cond-mat/0103487.
[3] T.A. Callcott et al.: Phys. Rev. B**64**, 132504 (2001)
[4] S.L. Bud'ko et al.: Phys. Rev. Lett. **86**, 1877 (2001).
[5] H. Schmidt et al.: Phys. Rev. B **63**, 220504 (2001).
[6] J. Kortus et al.: Phys. Rev. Lett. **86**, 4656 (2001).
[7] M. Imada, J. Phys. Soc. Jpn. **70**, 1218 (2001).
[8] K. Yamaji, J. Phys. Soc. Jpn. **70**, 1476 (2001).
[9] K. D. Belashchenko et al.: Phys. Rev. B **64**, 092503 (2001)
[10] G. Satta et al.: Phys. Rev. B **64**, 104507 (2001)
[11] J.M. An and W. E. Pickett, Phys. Rev. Lett. **86**, 4366 (2001).
[12] S. Suzuki et al.: J. Phys. Soc. Jpn. **70**, 1206 (2001).
[13] D. Kaczorowski et al.: cond-mat/0103571.
[14] V.A. Gasparov et al.: cond-mat/0104323.
[15] A.S. Cooper et al.: Proc. Nat. Acad. Sci. **67**, 313 (1970).
[16] J. Akimitsu et al., Abstract for 2001 Annual meeting of Physical Society of Japan, Vol 3. p.533.
[17] L. Leyarovskaya and E. Leyarovski, J. Less Common Met. **67**, 249 (1979).
[18] J. Nakamura et al., Phys. Rev. B **64**, 174504 (2001).

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